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(54) Title: IMPROVED ADDITIVE COMPOSITION FOR OIL WELL CEMENTING FORMULATIONS			
(57) Abstract An oil and gas well cementing composition has styrene/butadiene latex and a combination of nonionic and anionic surfactants for improved physical properties, especially fluid loss.			

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Improved additive composition for oil well cementing formulations

Field of the invention

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The present invention relates to a improved oil and gas well cementing composition having a synergistic combination of nonionic and anionic surfactants which in particular improves the fluid loss, free water and rheological properties and provides
10 good compressive strength of the resulting cementing composition. The invention also relates to the use of certain nonionic and anionic surfactants as additives for improving oil and gas well cementing compositions.

15 Background of the invention

The initial step in the recovery of hydrocarbons and gases from underground formations is the placement of the cement slurry, usually including cement, water and other additives, in the
20 annular space between the porous formation and the steel casing. The main purpose of the cement in this annular space is to support the casing and also restrict fluid movement between formations. This process is referred to as primary cementing. The most important requirements to insure a satisfactory cementing
25 job are that a highly homogenous cement is present in the annulus and that strong bonds develop between the rock formation, cement and steel casing.

In order for this to happen, one must insure that the composition
30 of the cement slurry pumped downhole does not change greatly during the whole cementing process. Therefore, contamination of the cement slurry by the drilling mud used in the previous operation or excessive loss of water to the formation must be carefully avoided. A well-formulated cement slurry will, therefore, exhibit
35 low fluid loss to the formation, give either zero or very low free water, have a viscosity low enough to be pumpable, set to a hardened mass within the desired time interval and provide adequate compressive strength to support the casing.

40 The free water of a slurry is simply the supernatant fluid formed on top of the slurry column which provides an indication of the amount of settling of the cement particles during slurry placement. Excessive free water on top of the cement column will result in an incompetent zone close to the top of the liner which
45 will have to be remedied with an expensive squeeze job. The viscosity of the slurry describes the rheological behavior of the slurry, which is determined by measuring the plastic viscosity

(pv) and the yield point (yp) of the slurry. The cement slurry should be fluid and pumpable until it is in place, then it should start to set as soon as possible after placement. Any delay in the development of compressive strength will increase the "waiting on cement" time (WOC) necessary before proceeding with the next operation. The thickening time (TT) is used to describe the point at which the gelation of the cement has proceeded to such an extent so as to affect the pumping rates.

- 10 Neat cement slurries have a fluid loss which varies from 700 to 2500 mL over a thirty minute period. This rate of loss will result in rapid dehydration and incorrect placement of the slurry and consequently will lead to failure of the whole cementing job. In order to attempt the control of fluid loss from the cement
- 15 slurry to the surrounding rock formation, the permeability of the cement matrix must be reduced. This is achieved by addition of additives which provide excellent fluid loss control but at the same time do not adversely affect other properties of the slurry, such as free water, rheology, thickening times and compressive
- 20 strength.

Commercial fluid loss additives based on cellulosic polymers such as hydroxyethylcellulose (HEC) provide fairly good fluid loss control but there are some obvious drawbacks associated with cel-

- 25 lulosic polymers. Typical loadings of these polymers to achieve good fluid loss control are in the range of 0.5 to 1% by weight of cement. Such high loadings results in a dramatic increase in the plastic viscosity and the yield point of the slurry, which translates to an increase in the energy needed to pump the slurry
- 30 downhole. This means that every improvement in the fluid loss brought about by an increase in the level of the cellulosic polymer has to be paid for with high pumping pressures. Other drawbacks of cellulosic polymers include retardation in the thickening times of slurries and also the instability of these polymers
- 35 at high temperatures, which limits their usefulness as a fluid loss additives to wells cooler than 93°C (200 degrees F.).

Synthetic polymers based on acrylamide and polyvinylpyrrolidone have been considered by the industry as additives for fluid loss

- 40 control in cement compositions, but they have not come into widespread use because of certain inherent drawbacks. Both acrylamide and polyvinyl pyrrolidone are prone to hydrolysis in the alkaline environment of the cement composition and therefore cause excessive retardation in the development of cement compressive
- 45 strength. Furthermore polyvinylpyrrolidone is expensive and has a strong flocculating behavior which makes it an unattractive candidate as an additive in cement compositions. The synthetic

polymers used as fluid loss additives are typically high molecular weight polymers which are quite expensive and this limits the amount of polymeric additive that can be added to the cement composition. Even if the cost factor is overlooked, high loadings of synthetic polymers may give improved fluid loss properties but often lead to viscous slurries which require increased pumping energy.

The art is replete with copolymers which function as additives in cement compositions, but the inherent drawbacks associated in the form of undesirable side effects in the case of cellulosic and some synthetic polymers, coupled with the high cost of synthetic polymers have severely curtailed their widespread use in the industry.

As heretofore noted, slurry compositions for oil and gas well cementing typically require that the slurry be fluid enough to be pumpable. This means that the plastic viscosity of the slurry should be less than 0.1 Pa·s (100 centipoises (cp)), and more preferably less than 0.05 Pa·s (50 cp). In addition, the yield point of the slurry should be less than 9.6 Pa (20 lbs/100 ft²), the fluid loss be less than 50 mL/30 minutes and the free water be less than or equal to 3 mL over a two hour standing period. Cementing compositions meeting these requirements can be extremely difficult to design, and often times do not meet all of these requirements.

Certain cementing compositions which contain anti-gas channeling additives have been described in the art. For example, Parcevaux et al., U.S. Patent No. 4,537,918, describes a cement composition which contains styrene-butadiene latex, as well as a stabilizer. The stabilizer is described as an anionic component of the cement composition which is selected from the group of lignosulfonates and their partly desulfonated derivative, sulfonic acid or sulfide modified melamine-formaldehyde resins, formaldehyde/sulfonate naphthalene resins, and condensation products of bi-nuclear sulfonated phenols and of formaldehyde. Each compound in this recited class of stabilizers is thus required to be anionic and to include a compound which contains sulfur in its molecule.

In Parcevaux et al., U.S. Patent No. 4,721,160, there is also described a cement slurry composition which contains a styrene butadiene latex and a stabilizer. However, the patentees limit their additive for use with a resulting cement composition having a specific gravity within the range of 1.2 to 1.6, i.e. a light-weight cement slurry composition.

In addition, U.S. Patent No. RE 28,722 reissued to Sanders, U.S. Patent No. 3,043,790, describes a cement mortar composition which includes a styrene butadiene additive system having three necessary additives. These include a nonionic surfactant, an 5 ionic surfactant and a polyorganosiloxane fluid surfactant. The preferred nonionic surfactants include condensation products of ethylene oxide with phenols, naphthols, and alkyl phenols, for example octyphenoxy-nonaoxyethyleneethanol. There appears to be no mention made of the use of this particular composition in oil 10 and gas well cementing applications.

There presently exists a need in the art for an additive system which is relatively inexpensive, and provides superior fluid loss control via a synergistic combination of nonionic and anionic 15 surfactants, without adversely affecting other critical properties of the cement slurry for oil and gas well cementing.

Objects of the invention

20 It is therefore an object of the present invention to provide a cementing composition for use in oil and gas wells which comprises a synergistic combination of nonionic and anionic surfactants which improves several of the physical properties of the cement composition.

25 It is also an object of the invention to provide for the use of certain nonionic and anionic surfactants as additives to improve cementing compositions used in the drilling industry.

30 Another object of the present invention is to utilize certain nonionic and anionic surfactants in combination with styrene-butadiene latex and cement which gives a readily mixable cement slurry for use in oil and gas wells.

35 A further object of the invention is to provide a cement composition having nonionic and anionic surfactant additives to achieve a set of rheological properties which makes it readily pumpable.

Still another object of the invention is to have an oil and gas 40 well cementing composition which gives very low fluid loss over a thirty minute interval.

Another object is to have a cementing composition which provides low free-water values.

45

A further object is to have a cement slurry composition which is not subject to excessive retardation, and which has good compressive strength.

5 Summary of the invention

These and other objects of the invention are achieved by providing an oil and gas well cementing composition which is made up of cement, and a styrene/butadiene latex in an amount of from about 5% to about 30% by weight of the dry cement, that is without water. The ratio of styrene to butadiene in the latex is typically about 2:1.

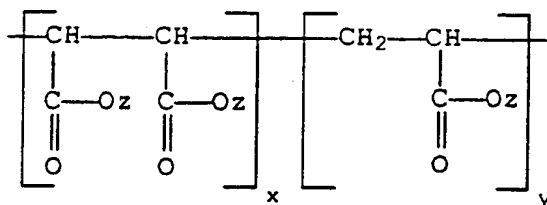
As part of the composition there is also from about 0.05% to about 2%, more preferably from about 0.08% to about 0.7%, and even more preferably from about 0.1% to about 0.5% of the non-ionic surfactant alkylphenol ethoxylate having a molecular weight of from about 1,000 to about 3,000 and having from about 25 to about 50 moles of ethylene oxide (EO) (n equals about 25 to about 50). The alkylphenol ethoxylate has the following formula:



where R is a butyl, pentyl, hexyl, heptyl, octyl, nonyl or decyl group. In a preferred embodiment of the invention, the alkylphenol ethoxylate has a molecular weight range of from about 1300 to about 2500, and even more preferably from about 1500 to about 2200. The moles of ethylene oxide (value of n) are preferably from about 28 to about 45, and even more desirably from about 30 to about 40. In an especially preferred embodiment, the molecular weight is about 1730 and the moles of EO are about 35. It is in this embodiment that the alkylphenol ethoxylate is octylphenol-ethoxylate.

In combination with the heretofore alkylphenol ethoxylate, there is also from about 0.01% to about 2% of one or more anionic surfactants from the following group of polymers:

- maleic acid/acrylic acid copolymers of the formula:

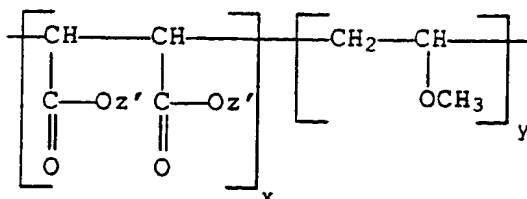


wherein z is an alkali metal, preferably sodium, or hydrogen, and wherein x and y are numbers such that the molecular weight of the copolymer is in the range of from about 4,000 to about 200,000;

5

- maleic acid/methyl vinyl ether copolymers of the formula:

10



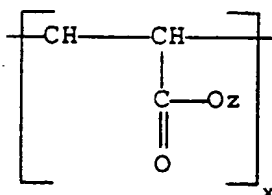
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wherein z' is an alkali metal, preferably sodium; and wherein x and y are numbers such that the molecular weight of the copolymer is in the range of from about 4,000 to about 200,000;

20

- polyacrylic acid homopolymers of the following formula:

25



wherein z is an alkali metal, preferably sodium, or hydrogen; and x is a number such that the molecular weight of the polymer is in the range of from about 500 to about 250,000;

30

- copolymers of maleic anhydride and 2-hydroxypropylacrylate, such that the copolymer has a molecular weight within the range of from about 1,000 to about 20,000.

- 35 Water makes up the remainder of the cement composition in an amount such that the total quantity of water is from about 30% to about 60% by weight of the dry cement. Unless otherwise specified, all quantities of individual components of the cement composition are expressed in terms of weight percentage based on the weight of the dry cement. All molecular weights are expressed as weight average molecular weight or M_w .

- 45 Further provided as part of the invention is the use of the heretofore described alkylphenol ethoxylates in combination with at least one of the heretofore described anionic surfactant additives as stabilizer additives in oil and gas well cementing compositions.

Also provided is a method of improving the rheological properties of cementing compositions which comprises adding the heretofore nonionic and anionic surfactant stabilizer additives in the quantities set forth.

5

It has now been discovered that the synergistic combination of alkylphenol ethoxylate with one or more of the heretofore anionic surfactants provides measurable improvements in the plastic viscosity, yield point, fluid loss, and free-water values, as well
10 as other physical properties of cement compositions used in drilling oil and gas wells. The nonionic and anionic surfactants as part of the invention function as stabilizers in the cement composition by stabilizing the styrene-butadiene dispersion. In this way, they provide a well dispersed cement matrix which
15 effectively controls the loss of fluid from the cement slurry composition.

Detailed description of the preferred embodiments

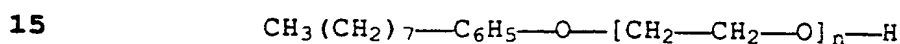
20 The cement utilized as part of the composition according to the invention is any of the known cements available to those skilled in the art of oil and gas well cementing. Of these, American Petroleum Institute (API) Class H is preferred. Particularly preferred is Taxis Lehigh Class H cement available from the Taxis
25 Lehigh Company of Buda, Texas.

The styrene/butadiene latex is added to the cement in an amount of from about 5% to about 30% based on the weight of the cement. In a preferred embodiment, the latex comprises from about 8% to
30 about 25%, most desirably, about 15%, by weight of the cement. The ratio of styrene to butadiene in the latex is typically about 2:1, although a somewhat higher or lower ratio is certainly within the scope of the invention. In most instances, a dispersion of about 50% of the active polymer styrene/butadiene is
35 formed with about 50% water, and this dispersion in turn is added to the cement.

Styrene/butadiene latexes are considered to be very compatible with cement. These latexes are typically manufactured via an
40 emulsion polymerization process to yield a dispersion with an average of about 50% latex polymer content, the remainder being water. Since these dispersions have a relatively high percentage of active polymer, it is possible to utilize a high loading in cement compositions in order to obtain a uniform well-dispersed
45 cement matrix. It is this cement matrix that effectively controls the loss of fluid from the cement composition. Since the styrene-butadiene polymer is dispersed in the aqueous medium, it is

possible to use high loadings of the polymer without imparting high viscosity to the cement slurry.

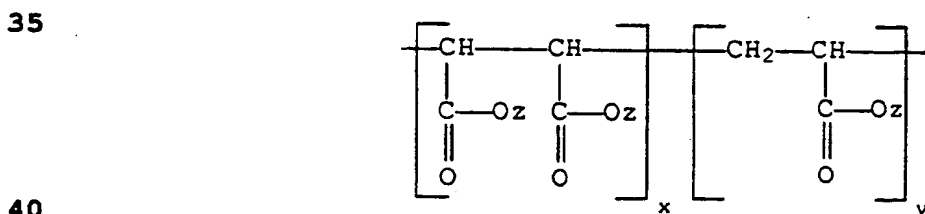
As part of the invention, there is also included a nonionic alkylphenol ethoxylate surfactant additive as a stabilizer. It is especially desirable that this surfactant be octylphenol ethoxylate with a molecular weight in the range of from about 1500 to about 2200, and having from about 30 to about 41 moles of ethylene oxide (EO). Especially preferred is octylphenol ethoxylate having a molecular weight of about 1730 and about 35 moles of EO. Octylphenol ethoxylate is octylphenol to which ethylene oxide is added. The octylphenol ethoxylate has the following formula:



wherein n has a value of from about 30 to about 41. This component is added in an amount of from about 0.05% to about 2% based on the weight of the cement. In a preferred embodiment, the octylphenol ethoxylate is added in an amount of from 0.08% to about 0.7%, even more preferably from about 0.1% to about 0.5%. Particularly preferred for use with the composition according to the invention is the octylphenol ethoxylate available from BASF Corporation and marketed under the tradename ICONOL® OP30 or 40. This product may also be known under the tradename TRITON® X 405, which is available from Union Carbide.

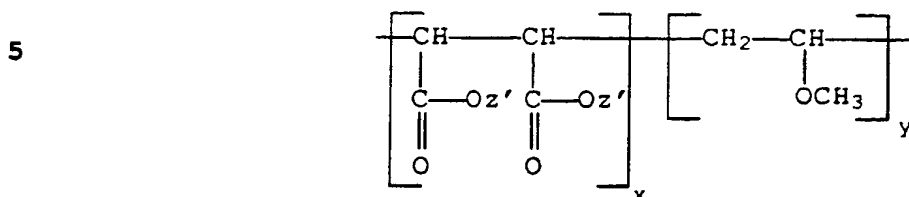
In combination with octylphenol ethoxylate is added about 0.01% to about 2% of one or more anionic surfactants from the following group of polymers:

- copolymers of maleic acid/acrylic acid of the following formula:



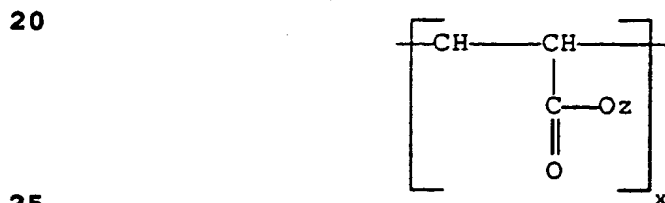
wherein z is an alkali metal, preferably sodium, or hydrogen. x and y are numbers such that the molecular weight of the copolymer is in the range of from about 4,000 to about 200,000, preferably about 30,000 to about 160,000, more preferably about 50,000 to about 140,000. Most preferably, the molecular weight of the anionic maleic acid/acrylic acid copolymer is about 70,000;

- copolymers of maleic acid/methyl vinyl ether of the following formula:



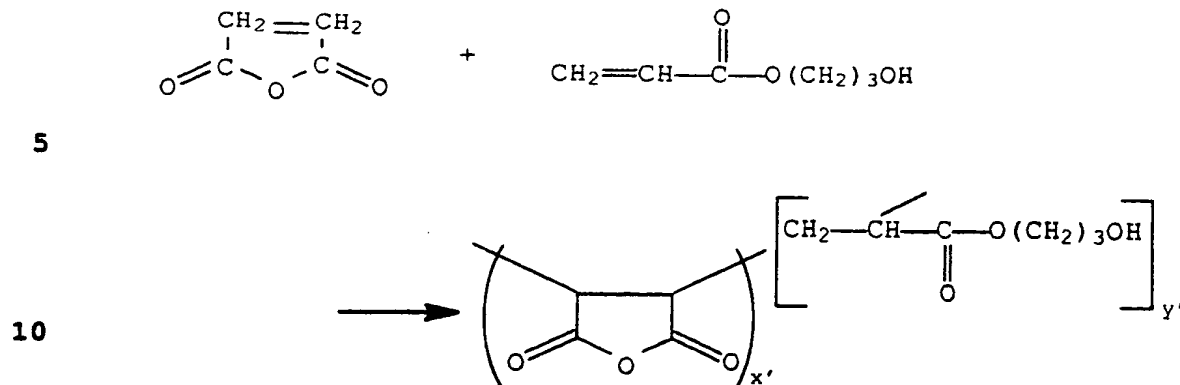
- 10 wherein z' is an alkali metal, preferably sodium. x and y are numbers such that the molecular weight of the copolymer is in the range of from about 4,000 to about 200,000, preferably about 30,000 to about 160,000, more preferably about 50,000 to about 140,000. Most preferably, the molecular weight of the anionic maleic acid/methyl vinyl ether copolymer is about 70,000;
- 15

- polyacrylic acid homopolymers of the following formula:



- wherein z is an alkali metal, preferably sodium or hydrogen. x is a number such that the molecular weight of the polymer is in the range of from about 500 to about 250,000, more preferably in the range of from about 1,000 to about 6,000 and 10,000 to about 150,000, and even more preferably from about 3,000 to about 4,000 and 15,000 to about 100,000. Particularly preferred is the anionic surfactant having a molecular weight of about 4,000 and about 15,000;
- 30

- 35 - copolymers having about five weight percent of 2-hydroxypropylacrylate and about ninety-five weight percent of maleic anhydride having a molecular weight within the range of from about 1,000 to about 20,000. More preferably, the molecular weight of the copolymer is in the range of from about 1,000 to about 8,000, and even more preferably from about 500 to about 2,000. Most preferably, the anionic surfactant copolymer additive has a molecular weight of about 1,200. This copolymer anionic surfactant has the following structural formula:
- 40
- 45



wherein x' is about 95% and y' is about 5% on a weight basis. These copolymers may be prepared in accordance with the teachings of Denzinger, U.S. Patent No. 5,073,269, Example 2, which is incorporated herein by reference.

The anionic copolymer(s) is added to the cement composition in amounts of from about 0.01 to about 2% by weight, preferably from about 0.03 to about 0.3%, and more preferably in the range of from about 0.05 to about 0.25%. In an especially preferred embodiment of the invention, the cement composition has about 0.08 to about 0.18% of anionic copolymer.

Water is also added to the cement composition in amounts of from about 30% to about 60%, preferably from about 36% to about 42%, and more preferably about 38% by weight of the cement.

One or more defoamers may also be added to the various embodiments of the cement composition as part of the invention. These are added for their deaerentrainment properties imparted to the resulting cementing composition. Any one of a number of defoamers available to those skilled in the art may be utilized. Preferred for use is the defoamer available from BASF Corporation under the trademark PLURACOL® 4010. This is a polypropylene glycol with an average molecular weight of about 3300. The defoamer is typically added to the composition in an amount of from about 0.01% to about 0.1% based on the weight of the cement.

In some instances certain other additives known as retarders or accelerators may be added to the cement composition to adjust the thickening time of the cement slurry for the drilling operation. Because "Waiting on Cement" (WOC) is very expensive these additives are often added in quantities of from about 0.5 to about 1.5%. U.S. Patent No. 4,527,918 describes many of the known accelerators and retarders available to those in the art, and the salient portions thereof are incorporated herein by reference.

Sometimes in addition to these additives, silica flour is added in amounts of from about 30% to about 35% by weight of the cement if the temperature of the oil well is greater than 104°C (220 F). Since Portland cement experiences strength retrogression at high temperatures, silica flour can be added to increase the compressive strength of cement.

- The physical properties of the cement slurry compositions according to the various embodiments of the invention should be as follows: the fluid loss should be less than about 55 mL/30 minutes, preferably less than about 50 mL/30 minutes, and more preferably less than about 40 mL/30 minutes. The plastic viscosity of the composition should be less than about 0.1 Pa·s (100 cp), and more preferably less than about 0.05 Pa·s (50 cp). Additionally, the yield point should be less than about 9.6 Pa (20 lbs/100 ft²). The free-water value should be less than or equal to about 3 mL for a two hour standing period, preferably less than about 2 mL, and more preferably less than about 1 mL.
- The following example will illustrate how to make the cement composition according to one embodiment of the invention. This example should not be construed as limiting the scope of the invention.

Example 1

- To a Waring blender, approximately 327 mL of water is added. Next, about 0.35 grams of defoaming agent and 1.3 grams of the nonionic surfactant TRITON X 405 are added and this mixture is allowed to stir at low speed (1,000 rpm). If the anionic surfactant stabilizer is liquid, approximately 1.3 grams is also added along with the TRITON X 405 at this point. Next, approximately 131 grams of styrene/butadiene latex is added. If the second stabilizer is a solid it is first blended with about 860 grams of dry cement and the resulting mixture is added to the solution within 10 seconds with the stirring maintained at 4,000 rpm. Soon after the cement mixture is added, stirring is increased to 12,000 rpm and the mixture is allowed to stir for 35 seconds after which stirring is stopped. Rheology measurements are made at room temperature after which the slurry is homogenized in an atmospheric consistometer for twenty minutes at the desired operating temperature. The pourability of the slurry is determined at this point. If after twenty minutes of stirring the resulting slurry is so thick that it does not pour out of the consistometer, then the slurry is discarded and no further tests are performed. If the slurry is homogenous and pourable then routine cement testing is then performed.

Example 2

The following API Tests at the indicated temperatures were performed with the composition according to various embodiments of the invention. The compositions performed extremely well based upon several measurable parameters. These tests further highlight the use of the nonionic and anionic surfactant stabilizer additives as part of the cement compositions according to the invention. Measurements were based on the following:

10

Fluid loss:

Thirty minute fluid-loss values were measured under static conditions using a high temperature, high pressure filter press made by Bariod. All tests were conducted at 68.9 bar (1,000 psi) using nitrogen as the pressurizing gas.

Free water:

20 The amount of free water was determined by measuring the amount of water present of top of a 250 mL graduated cylinder filled with cement slurry, after a two hour standing period at room temperature.

25 Rheology:

Rheological properties were measured using Chan 35 Viscometer equipped with a R1 rotor sleeve and a B1 bob. All measurements were made at room temperature on freshly prepared slurries.

30

Thickening Time:

Atmospheric thickening times were measured with a Chandler atmospheric consistometer set to the desired test temperature.

35 The reported value indicated the length of time taken by the slurry to achieve a consistency of 70 Bc.

Compressive Strength:

40 The slurries were cured in a pressurized curing chamber and the compressive strength of the cured cement was tested by crushing the 2.54 cm by 2.54 cm (2 inch by 2 inch) cement cubes with a Soiltest hydraulic press with a gage measuring up to 1,378 bar (20,000 psi).

45

Latex Loadings:

- 15.3% BWOC (1.73 gallons/sack) (BWOC = Based on Weight of Cement)
10.2% BWOC (1.15 gallons/sack)
5 8.1% BWOC (0.92 gallons/sack)

Those skilled in the art may find that the loading of latex may vary somewhat depending upon individual oil well conditions.

- 10 2.1 API Test at 82°C (180 degrees F) (with maleic acid/acrylic acid copolymer anionic surfactant having a M_w of about 70,000)

Cement Slurry Composition

- 15 (% Based on Weight of Cement, or BWOC):

Texas Lehigh Class H Cement: 860 grams
Styrene/Butadiene Latex: 15.3%
Defoamer: 0.04%
Water: 38%

- 20 TRITON X 405: 0.153%
maleic/acrylic acid copolymer: 0.153%

API Fluid loss at 30 minutes: 36 mL
Free water: 2 mL
25 Plastic Viscosity (Pa·s): 0.028 (28 cp)
Yield Point (Pa): 8.93 (18.6 lbs/100 ft²)
Atmospheric Thickening Time: 161 minutes
Compressive Strength: 213 bar (3087 psi)

- 30 2.2 API Test at 82°C (180 degrees F) (with maleic acid/acrylic acid copolymer anionic surfactant having a M_w of about 70,000)

Cement Slurry Composition

- 35 (% Based on Weight of Cement, or BWOC):

Texas Lehigh Class H Cement: 860 grams
Styrene/Butadiene Latex: 15.3%
Defoamer: 0.04%
Water: 38%

- 40 TRITON X 405: 0.153%
maleic/acrylic acid copolymer: 0.0153%

API Fluid loss at 30 minutes:	55 mL
Free water:	3 mL
Plastic Viscosity (Pa·s):	0.03 (30 cp)
Yield Point (Pa):	8.69 (18.1 lbs/100 ft ²)
5 Atmospheric Thickening Time:	156 minutes
Compressive Strength:	173 bar (2512 psi)

The above test demonstrates that reducing the anionic surfactant concentration by ten fold does not result in any significant
10 reduction in the performance.

2.3 API Test at 82°C (180 degrees F) (maleic acid/acrylic acid copolymer from 2.1/2.2 above except that carboxylate groups are fully neutralized)

15

Cement Slurry Composition	
(% Based on Weight of Cement, or BWOC):	
Texas Lehigh Class H Cement:	860 grams
Styrene/Butadiene Latex:	15.3%
20 Defoamer:	0.04%
Water:	38%
TRITON X 405:	0.153%
maleic/acrylic acid copolymer:	0.153%

25 API Fluid loss at 30 minutes:	34 mL
Free water:	1 mL
Plastic Viscosity (Pa·s):	0.027 (27 cp)
Yield Point (Pa):	7.68 (16.0 lbs/100 ft ²)
Atmospheric Thickening Time:	157 minutes
30 Compressive Strength:	183 bar (2666 psi)

2.4 API Test at 82°C (180 degrees F) (with maleic acid/methyl vinyl ether copolymer anionic surfactant having a M_w of about 70,000 as part of the invention)

35

Cement Slurry Composition	
(% Based on Weight of Cement, or BWOC):	
Texas Lehigh Class H Cement:	860 grams
Styrene/Butadiene Latex:	15.3%
40 Defoamer:	0.04%
Water:	38%
TRITON X 405:	0.153%
anionic surfactant:	0.153%

45

API Fluid loss at 30 minutes: 32 mL
Free water: 2 mL
Plastic Viscosity (Pa·s): 0.036 (36 cp)
Yield Point (Pa): 11.2 (23,4 lbs/100 ft²)
5 Atmospheric Thickening Time: 168 minutes
Compressive Strength: 181 bar (2627 psi)

2.5 API Test at 82°C (180 degrees F) (with polyacrylic acid homo-
polymer anionic surfactant where z is H and having a M_w of
10 about 4,000 as part of the invention)

Cement Slurry Composition

(% Based on Weight of Cement, or BWOC):

Texas Lehigh Class H Cement: 860 grams
15 Styrene/Butadiene Latex: 15.3%
Defoamer: 0.04%
Water: 38%
TRITON X 405: 0.153%
anionic surfactant: 0.153%

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API Fluid loss at 30 minutes: 31 mL
Free water: 1 mL
Plastic Viscosity (Pa·s): 0.021 (21 cp)
Yield Point (Pa): 1.01 (2.1 lbs/100 ft²)
25 Atmospheric Thickening Time: >450 minutes

2.6 API Test at 82°C (180 degrees F) (with the polyacrylic acid
homopolymer anionic surfactant as part of the invention)

30 Cement Slurry Composition

(% Based on Weight of Cement, or BWOC):

Texas Lehigh Class H Cement: 860 grams
Styrene/Butadiene Latex: 15.3%
Defoamer: 0.04%
35 Water: 38%
TRITON X 405: 0.153%
anionic surfactant: 0.153%

API Fluid loss at 30 minutes: 58 mL
40 Free water: 2 mL
Plastic Viscosity (Pa·s): 0.024 (24 cp)
Yield Point (Pa): 1.53 (3.2 lbs/100 ft²)

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2.7 API Test at 82°C (180 degrees F) (with copolymer anionic surfactant additive of maleic acid anhydride and 2-hydroxypropylacrylate having a M_w of about 1,200 according to the invention)

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Cement Slurry Composition

(% Based on Weight of Cement, or BWOC):

Texas Lehigh Class H Cement:	860 grams
Styrene/Butadiene Latex:	15.3%
10 Defoamer:	0.04%
Water:	38%
TRITON X 405:	0.153%
anionic surfactant:	0.0765%
15 API Fluid loss at 30 minutes:	34 mL
Free water:	3 mL
Plastic Viscosity (Pa·s):	0.022 (22 cp)
Yield Point (Pa):	2.3 (4.8 lbs/100 ft ²)
Atmospheric Thickening Time:	325 minutes

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These results demonstrate that fluid loss values are mostly lower than 50 mL for a typical latex loading of 1.73 gallons/sack of a temperature of 82°C (180 F). The free-water values are consistently lower than or equal to 3 mL at the temperature set forth above. Plastic viscosity values are lower than 0.05 Pa·s (50 cps), and the yield point values are below 12.0 Pa (25 lbs/100 ft²). A good set of compressive strength properties was observed with Class H cement at 82°C (180 F).

30 Example 3

In order to fully assess the efficacy of the cement composition according to the invention, comparative tests were done utilizing:

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3.1 no surfactant stabilizer additive

3.2 formaldehyde/sulfonate naphthalene resin alone (anionic surfactant disclosed in U.S. Patent No. 4,537,918)

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3.3 TRITON X 405 nonionic surfactant alone

3.4 TRITON X 405 nonionic surfactant with 3.2 above

45 3.5 anionic surfactant from 2.1 above alone

3.6 anionic surfactant from 2.3 above alone

3.7 anionic surfactant from 2.4 above alone

5 3.8 anionic surfactant from 2.5 above alone

3.9 anionic surfactant from 2.6 above alone

In each test, 860 grams of Taxis Lehigh Class H Cement was
10 utilized. 15% of styrene/butadiene latex, 0.04% of defoamer, and
38% of water was also utilized (all %'s BWOC). The fluid-loss
values were as follows at 82°C (180 degrees F):

API Fluid Loss at 30 minutes:

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3.1 no surfactant stabilizer additive - fluid loss could not be
measured as cement slurry could not be poured.

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3.2 0.153% sodium naphthalene sulfonic acid condensate with
formaldehyde alone (anionic surfactant disclosed in U.S.
Patent No. 4,537,918) - fluid loss was 138 mL.

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3.3 0.153% TRITON X 405 nonionic surfactant alone - fluid loss
was 130 mL.

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3.4 0.153% TRITON X 405 nonionic surfactant with 1% 2) above -
fluid loss was 112 mL.

3.5 0.153% anionic surfactant from 2.1 above alone - fluid loss
was 146 mL.

3.6 0.153% anionic surfactant from 2.3 alone - fluid loss was
135 mL.

35 3.7 0.153% anionic surfactant from 2.4 alone - fluid loss was
138 mL.

3.8 0.153% anionic surfactant from 2.5 alone - fluid loss was
150 mL.

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3.9 0.153% anionic surfactant from 2.6 alone - fluid loss was
126 mL.

Examples 2 and 3 demonstrate the synergistic interaction between
45 the nonionic and anionic surfactants as part of the claimed
invention according to the various embodiments thereof. These
surfactant additives lead to the stabilization of the styrene/

butadiene dispersions in the cement matrix. By virtue of this stabilization, a compact cement matrix is formed which controls the loss of fluid from the cement slurry.

5 While the invention has been described in each of its embodiments, it is expected that certain modifications thereto may be made by those skilled in the art without departing from the true spirit and scope of the invention, as set forth in the specification and the accompanying claims.

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Claims:

1. An oil and gas well cementing composition, comprising:

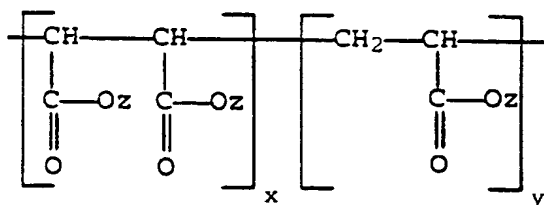
- a) cement;
- b) styrene/butadiene latex in an amount of from about 5% to about 30% by weight of said cement;
- c) from about 0.05% to about 2% by weight of the nonionic surfactant stabilizer additive alkylphenol by weight of the nonionic surfactant stabilizer additive alkylphenol ethoxylate of the following formula:



where R is butyl, pentyl, hexyl, heptyl, octyl, nonyl or decyl, said alkylphenol ethoxylate having a molecular weight of from about 1,000 to about 3,000 such that n equals from about 25 to 50;

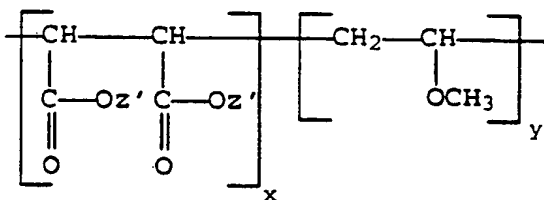
- d) from about 0.01% to about 2% by weight of at least one anionic surfactant stabilizer additive selected from the following group of polymers:

- maleic acid/acrylic acid copolymers having the following formula:



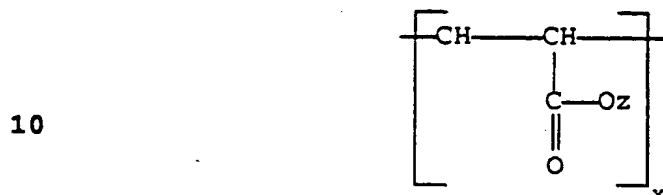
wherein z is an alkali metal or hydrogen, and x and y are numbers such that the molecular weight of the said copolymer is from about 4,000 to about 200,000;

- maleic acid/methyl vinyl ether copolymers having the following formula:



wherein z' is an alkali metal, and x and y are numbers such that the molecular weight of the said copolymer is from about 4,000 to about 200,000;

- 5 - polyacrylic acid homopolymers of the following formula:



15 wherein z is an alkali metal or hydrogen; and x is a number such that the molecular weight of the said polymer is from about 500 to about 250,000;

- 20 - copolymers of maleic anhydride and 2-hydroxypropyl-acrylate, such that the molecular weight of said copolymer is from about 1,000 to about 20,000;

- 25 e) water in an amount such that the total quantity of water is from about 30% to about 60% by weight of said cement.
- 30 2. The composition as claimed in claim 1, wherein said additive c) is present in an amount of from about 0.1 to about 0.5%.
3. The composition as claimed in claim 1 and 2, wherein said additive d) is present in an amount of from about 0.08 to about 0.18%.
4. The composition as claimed in claims 1 to 3, further comprising one or more defoamers in an amount of from about 0.01 to about 0.1% based on the weight of said cement.
- 35 5. The composition as claimed in claims 1 to 4, said composition having a fluid loss of less than or equal to about 50 mL/30 minutes.
- 40 6. The composition as claimed in claims 1 to 5, said composition having a plastic viscosity of less than or equal to about 0,1 Pa·s (100 centipoises).
- 45 7. The composition as claimed in claims 1 to 6, said composition having a free-water value of less than or equal to about 3 mL over an approximately 2 hour standing period.

8. The composition as claimed in claims 1 to 7, said composition having a yield point value of less than or equal to 9.6 Pa (20 lbs/100 ft²).
- 5 9. The composition as claimed in claims 1 to 8, wherein said alkylphenol ethoxylate has a molecular weight range of from about 1,300 to about 2,500, and n equals from about 28 to about 45.
- 10 10. A method of improving the rheological properties of oil well cementing compositions which comprises adding the stabilizer additives c) and d) of claim 1.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/02348

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 E21B33/13 C04B28/02 C04B24/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 E21B C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 537 918 (P.A.PARCEVAUX) 27 August 1985 cited in the application see claim 1 ---	1
A	US,A,4 721 160 (P.A.PARCEVAUX) 26 January 1988 cited in the application see claim 1 ---	1
A	US,A,3 043 790 (P.F.SANDERS) 10 July 1962 cited in the application see claims 1-4 ---	1,9
A	US,A,3 943 083 (S.L.ADAMS) 9 March 1976 see column 6, line 67 - column 7, line 17; claim 1 --- -/-	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/02348

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US,A,2 614 998 (P.J.LEA) 21 October 1952 see claim 1</p> <p>-----</p>	1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 93/02348

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4537918	27-08-85	FR-A- 2524460	07-10-83
		FR-A- 2539735	27-07-84
		AU-B- 573522	16-06-88
		AU-A- 1305583	13-10-83
		CA-A- 1217038	27-01-87
		DE-A- 3377058	21-07-88
		EP-A, B 0091377	12-10-83
		JP-B- 1004977	27-01-89
		JP-C- 1522788	12-10-89
		JP-A- 59045951	15-03-84
		OA-A- 7391	30-11-84
US-A-4721160	26-01-88	FR-A- 2573064	16-05-86
		DE-A- 3564559	29-09-88
		EP-A, B 0183296	04-06-86
US-A-3043790		NONE	
US-A-3943083	09-03-76	CA-A- 1051650	03-04-79
		US-A- 3993134	23-11-76
US-A-2614998		NONE	